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(54) Title: **METHOD AND COMPOSITION FOR THE GRADUAL PERMANENT COLORING OF HAIR**

(57) Abstract: A method for permanently dyeing hair which comprises subjecting said hair to a number of treatments, having a set time interval between each two consecutive such treatments, wherein each treatment comprises steps a.) and b.) below: a.) contacting said hair, for a period of about 5 seconds to about 5 minutes with a recently made mixture of: i.) an alkaline composition comprising a dye intermediate in a shampoo base or in a conditioner base; and ii.) an acidic composition comprising an oxidating compound in a shampoo base or in a conditioner base; b.) rinsing said mixture from said hair with water; with the proviso that when a conditioner base is present in a.) i.) above, an independently selected conditioner base is also present in a.) ii.) above; and when a shampoo base is present in a.) i.) above, an independently selected shampoo base is also present in a.) ii.) above; and wherein said number of treatments is between about 2 to about 30; and wherein said set time interval between each two consecutive treatments is between about 8 hours and 30 days, is described.

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METHOD AND COMPOSITION FOR THE GRADUAL  
PERMANENT COLORING OF HAIR

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BACKGROUND OF THE INVENTION

The present invention relates to a method for the permanent  
10 coloring of hair with longer lasting conditioning and with  
minimized hair damage.

Most hair coloring products fall under three major  
groupings:

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1. Temporary hair color
2. Semi permanent hair color
3. Permanent hair color

20 Temporary color is a leave on product that causes minimal  
damage to the hair. However, temporary color causes stains,  
and leaches out under rain or with perspiration. Temporary  
color washes out with the next shampoo. Temporary color  
also does not give any control to the consumer over the  
25 amount of color deposited or the permanency of the color  
supplied. Temporary color does not result in a wide variety  
of colors and it has only a limited appeal.

Semi-permanent hair color comes as a rinse, and it causes  
30 minimal damage to the hair. However, semi-permanent hair  
color washes out to some degree with each shampoo and washes

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out completely within about 4 to 6 shampoos. Semi permanent hair color does not give the consumer any control regarding the amount of color deposited or the permanency of the color. Semi-permanent hair color has limited popularity  
5 with consumers.

Permanent hair color generally comes in two parts: a dye solution and a developer solution. Because of the damaging nature of current permanent dye treatments, most home  
10 coloring products come with a post treatment conditioner. In a permanent hair coloring treatment, the dye solution and the developer solution are mixed and then applied to the hair, which is then left for about 25 to about 35 minutes. The hair is then rinsed with water, treated with a post  
15 treatment conditioner, and then rinsed again with water.

The application of the dye solution and the developer solution affords permanent hair coloring. However, this method does not provide any conditioning benefit. The  
20 conditioning benefit comes through application of the post treatment conditioner, and it is only temporary. The conditioning benefit is lost with the next shampoo. Moreover, with permanent hair coloring treatments, shampooing the hair is usually not recommended after said  
25 treatments. Thus, hair is left feeling dirty, and can stain towels and pillows.

Coloring products need to be applied every four to six weeks since hair grows out of the scalp at the rate of  
30 approximately one half inch per month. Each coloring application causes damage to the hair, and that damage is

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cumulative. Hair touch ups after the initial treatment would also damage hair more.

It would be desirable to develop a method for permanently  
5 coloring hair that conditions hair, gives hair a soft clean feel, and minimizes the damage caused to hair by the coloring process. The present invention provides such a method.

10 Conventional hair coloring products cannot be used safely in the shower. It is an object of this invention to develop a method for permanently coloring hair, which can be carried out safely in the shower. It is also an object of the  
15 invention to provide a method for permanently coloring hair wherein the user has control of the amount of durable color deposited without hair damage. It is also an object of the invention to provide a method for permanently coloring hair wherein the user has control on the amount of  
20 lifting/lightening without causing hair damage. It is also an object of the invention to provide a method for permanently coloring hair wherein the user can employ the product as her daily hair care product to avoid new out growth of uncolored hair. It is also an object of the  
25 invention to provide a method for permanently coloring hair wherein said method involves less mess and difficulty than conventional permanent hair coloring methods. It is also an object of the invention to provide a method for permanently coloring hair wherein said method brings about gradual color changes with each application. Since gradual color changes  
30 are to occur, such a method would be virtually mistake-free because the consumer could stop or alter the coloring method

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if he or she did not like the course the hair coloring was taking. It is also an object of the invention to provide a method for permanently coloring hair wherein the amount of hair coloring composition employed can be varied from application to application in order to adjust the hair coloring results.

These and other aspects of this invention will become evident by a detailed description of the invention given below.

Patents related to the field of this invention are as follows:

U.S. Patent No. 4,104,021 which discloses a process in which human hair is dyed in successive treatments at selected intervals with oxidation colors (aromatic primary amines and amino phenols) admixed in each treatment with an oxidizing agent ( $H_2O_2$  or a derivative thereof) -- the quantity of oxidation colorant applied in each treatment being substantially the same and the quantity of oxidizing agent being increased from the first to the last treatment to effect a gradual increase in depth of shade - the mixture being allowed to remain on the hair for substantially the same time in each treatment, followed by removal by rinsing.

U.S. Patent 4,529,404 discloses an autoxidizable hair dye preparation capable of coloring or darkening hair when applied thereto and exposed to the atmosphere comprising a mixture of (I) at least one p-phenylene diamine compound, or

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An acid addition salt thereof, and (II) at least one 1,2,4-benzenetriol compound, each compound optionally containing nuclearly substituted C<sub>1-4</sub> alkyl, alkoxy, hydroxyalkyl or halogen. The preparation is preferably applied and exposed  
5 to the atmosphere repeatedly until the desired degree of darkening or color build-up is attained.

The preparations of this invention may also contain known additives or assistants such as hair grooming agents, for  
10 example quaternized vinyl pyrrolidone copolymers, carboxyvinyl polymers and the like, plasticizers, conditioners, thickeners, slip and wetting agents such as polyoxyethylenated fatty (e.g. lauryl) alcohols, stearyldimethylammonium chloride, silicone copolymer, foam  
15 boosters, preservatives, perfumes and the like.

U.S. Patent 5,968,486 describes a shampoo composition for lightening and highlighting hair which comprises

- 20           (i)           a peroxygen compound; and  
             (ii)           an anionic sulfonate;

said composition having a pH less than 5. There is also  
25 described an invention directed to a method for lightening and highlighting hair which comprises shampooing the hair with a lightening and highlighting effective amount of a composition of the invention.

30 Co-pending and commonly assigned U.S patent application Serial No. 09/558,235, filed April 24, 2000 discloses a hair

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conditioning composition for conditioning, lightening, and  
highlighting hair, which comprises

- i) peroxygen compound, and
- ii) a conditioning agent,

5 said composition having a pH of 5 or less.

#### SUMMARY OF THE INVENTION

The invention relates to a method for achieving permanent  
10 desired hair color change through the use of daily hair care  
compositions. The daily hair care compositions comprise a  
mixture of two compositions, part A and part B as described  
just below:

15 Part A: Dye intermediates in a conditioner or shampoo  
base at alkaline pH

Part B: Hydrogen peroxide in a conditioner or shampoo  
base at acidic pH

20 The present invention relates to specific compositions which  
are a mixture of part A' and part B' as described just  
below.

25 Part A: Dye intermediates in a conditioner or shampoo  
base at alkaline pH

Part B: Hydrogen peroxide in a conditioner or shampoo  
base at acidic pH

In the case of compositions in a conditioner base, Part  
30 A comprises from

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- a) about 0.1 to about 99.9% of a conditioning base, wherein the conditioning agent within said conditioning base comprises from about 0.5 to about 10% of the total composition;
- 5 b) about 0.1 to about 5% of oxidation dyestuffs;
- c) about 0.1 to about 5% of a coupling compound.

Unless indicated otherwise, all percentages used herein are percentages by weight of active material based on the weight  
10 of the respective composition.

More preferably, in the case of compositions in a conditioner base, part A can comprise from

- a) about 1 to about 5 % of a conditioning agent;
- 15 b) about 0.1 to about 0.5 % of dye;
- c) about 0.1 to about 1% coupling compound.

For compositions in a conditioner base, Part B comprises  
20 from:

- a) about 1 to about 5 % of a conditioning agent; and
- b) about 1 to about 5 % of an oxidizing compound.

For compositions in a shampoo base part A comprises:

- 25 a) about 0.1 to about 99.9% of a shampoo base, wherein the detergent foaming agent within said shampoo base comprises from about 0.5 to about 50% of the total composition % of a shampoo agent;
- b) about 0.1 to about 5% of oxidation dyestuffs;
- 30 c) about 0.1 to about 5% of a coupling compound.



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More preferably, in the case of compositions in a shampoo base, part A can comprise from

- a) about 2 to about 50 % (eg, about 2 to about 15 %) of a detergent foaming agent;
- 5 b) about 0.1 to about 0.5 % of dye;
- c) about 0.1 to about 1% coupling compound.

For compositions in a shampoo base part B comprises:

- a) about 0.5 to about 50% (eg, about 2 to about 50 %) of a detergent foaming agent; and
- 10 b) about 1 to about 5 % (eg, about 2 to about 5 %) of an oxidizing compound.

More preferably, in the case of compositions in a shampoo base, part A can comprise from

- 15 a) about 1 to about 15% of a detergent foaming agent; and
- b) about 1 to about 5 % of an oxidizing compound.

20 Specific preferred conditioner bases of the invention, part A, comprise about 0.5 to about 5% of a quaternary nitrogen-containing conditioning agent having two long aliphatic chains each of which contains about 12 to about 18 carbons and two short chain alkyl groups having one or two carbon  
25 atoms each bonded to quaternary nitrogen, 10% higher molecular weight fatty alcohols such as cetyl alcohol and stearyl alcohol; and about 1% to about 4% of a volatile silicone such as dimethicone and the dyestuff...

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Shampoo compositions of the invention comprise from about 0.5 to about 50% of an anionic surfactant or an amphoteric surfactant or mixtures thereof.

- 5 Conditioning compositions of the present invention comprise a mixture of part A and part B wherein:

Part A comprises:

- 10 a) about 0.1% to about 99.9% of a conditioning base, which comprises about 0.05% to about 10% of a conditioning agent based upon the total composition;
- b) about 0.1% to about 1% of a dye; and
- c) a volatile silicone;

15

Part B comprises:

- a) about 1 to about 5% of a conditioning base;
- b) about 1 to about 5% of an oxidative compound.

- 20 A conditioning composition of the invention is a composition as described just above, which further comprises in part A, part B, or part A and part B, a thickener which is a high molecular weight fatty alcohol wherein said high molecular weight fatty alcohol is selected from the group consisting
- 25 of cetyl alcohol and stearyl alcohol.

A shampoo composition for permanently dying hair comprises a mixture of

Part A and part B wherein:

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Part A comprises:

- 10 -

- a) about 0.1% to about 99.9% of a shampoo base; and
- b) about 0.1% to about 1% of a dye;

Part B comprises:

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- a) about 1 to about 5% of a shampoo base;
- b) about 1 to about 5% of an oxidative compound.

10 A shampoo composition of the invention is as described just above wherein said shampoo base in part A comprises about 5 to about 50%, based on the total part A composition, of an anionic surfactant, an amphoteric surfactant, or a mixture of an anionic surfactant and an amphoteric surfactant.

15 What follows is a description of the ingredients that can be included in the compositions of the present invention.

#### HAIR DYES AND HAIR COLORING AGENTS

20 The part A compositions of the present invention include as an essential feature one or more oxidative hair coloring agents. These hair coloring agents are present in compositions of the present invention which have a conditioner base, and compositions of the present invention  
25 which have a shampoo base. Such oxidative hair-coloring agents are used in combination with the oxidizing systems of the present invention to formulate permanent hair dye compositions.

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Permanent hair dye compositions as defined herein are compositions, which once applied to the hair, are substantially resistant to washout.

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#### OXIDATIVE DYES

The dye forming intermediates used in oxidative dyes are essentially aromatic diamines, aminophenols and their derivatives. These dye forming intermediates can be classified as; primary and secondary intermediates, couplers and modifiers, and nitro dyes. Primary intermediates are chemical compounds, which by themselves will form a dye upon oxidation. The secondary intermediates, also known as color modifiers or couplers and are used with other intermediates for specific color effects or to stabilize the color. Nitro dyes are unique in that they are direct dyes, which do not require oxidation to dye the hair.

The oxidation dye intermediates, which are suitable for use in the compositions and processes herein include aromatic diamines, polyhydric phenols, aminophenols and derivatives of these aromatic compounds (e.g., N-substituted derivatives of the amines, and ethers of the phenols). Primary oxidation dye intermediates are generally colorless molecules prior to oxidation. The oxidation dye color is generated when the primary intermediate is 'activated' and subsequently enjoined with a secondary intermediate (coupling agent), which is also generally colorless, to form a colored, conjugated molecule. In general terms, oxidation hair dye precursors or intermediates include those monomeric

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materials which, on oxidation, form oligomers or polymers having extended conjugated systems of electrons in their molecular structure. Because of the new electronic structure, the resultant oligomers and polymers exhibit a shift in their electronic spectra to the visible range and appear colored. For example, oxidation dye precursors capable of forming colored polymers include materials such as aniline, which has a single functional group and which, on oxidation, forms a series of conjugated imines and quinoid dimers, trimers, etc. ranging in color from green to black. Compounds such as p- phenylenediamine, which has two functional groups, are capable of oxidative polymerization to yield higher molecular weight colored materials having extended conjugated electron systems. Color modifiers (couplers), such as those detailed hereinafter, are preferably used in conjunction with the oxidation dye precursors herein and are thought to interpose themselves in the colored polymers during their formation and to cause shifts in the electronic spectra thereof, thereby resulting in slight color changes. A representative list of oxidation dye precursors suitable for use herein is found in Sagarin, "Cosmetic Science and Technology," Interscience, Special Edition, Volume 2, pages 308 to 310.

It is to be understood that the oxidizing aids of the present invention are suitable for use (in combination with a source of peroxide as detailed herein) with all manner of oxidation dye precursors and color modifiers and that the precursors detailed below are only by way of example and are not intended to limit the compositions and processes herein.

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The typical aromatic diamines, polyhydric phenols, aminophenols, and derivatives thereof, described above as primary dye precursors can also have additional substituents on the aromatic ring, e.g. halogen, aldehyde, carboxylic additional substituents on the amino nitrogen and on the phenolic oxygen, e.g. substituted and unsubstituted alkyl and aryl groups.

The hair coloring compositions of the present invention may, in addition to the essential oxidative hair-coloring agents, optionally include non-oxidative and other dye materials. Optional non-oxidative and other dyes suitable for use in the hair coloring compositions and processes according to the present invention include semi-permanent, temporary and other dyes. Non-oxidative dyes as defined herein include the so-called 'direct action dyes', metallic dyes, metal chelate dyes, fiber reactive dyes and other synthetic and natural dyes. Various types of non-oxidative dyes are detailed in: Chemical and Physical Behaviour of Human Hair` 3rd Edn. by Clarence Robbins (pp 250-259); 'The Chemistry and Manufacture of Cosmetics`. Volume IV. 2nd Edn. Maisson G. De ` Navarre at chapter 45 by G. S. Kass (pp 841-920); 'cosmetics: Science and Technology` 2nd Edn, Vol II Balsam Sagarin, Chapter 23 by F. E. Wall (pp 279-343); 'The Science of Hair Care` edited by C. Zviak, Chapter 7 (pp 235-261) and 'Hair Dyes`, J. C. Johnson, Noyes Data Corp., Park Ridge, U. S.A. (1973), (pp 3-91 and 113-139).

Specific hair dyes which may be included in the compositions of the invention include m-aminophenol, p-phenylene diamine, p-toluenediamine; p-phenylenediamine; 2-chloro-p-

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phenylenediamine; N-phenyl-p-phenylenediamine; N-2-methoxyethyl-p-phenylenediamine; N,N-bis-(hydroxyethyl)-p-phenylenediamine; 2-hydroxymethyl-p-phenylenediamine; 2-hydroxyethyl-p-phenylenediamine; 4, 4'-diaminodiphenylamine; 5 2,6-dimethyl-p-phenylenediamine; 2-isopropyl-p-phenylenediamine; N-(2-hydroxypropyl)-p-phenylenediamine; 2-propyl-p-phenylenediamine; 1,3-N, N-bis-(2-hydroxyethyl)-N, N-bis (4-aminophenyl)- 2-propanol; 2-methyl-4-dimethylaminoaniline; p-aminophenol; p- methylaminophenol; 10 3-methyl-p-aminophenol; 2-hydroxymethyl-p-aminophenol; 2-methyl-p-aminophenol; 2-(2-hydroxyethylaminomethyl)-p-aminophenol; 2-methoxymethyl-p-aminophenol; and 5-aminosalicylic acid; catechol; pyrogallol; o-aminophenol; 2, 4-diaminophenol; 2,4,5-trihydroxytoluene; 1,2,4- 15 trihydroxybenzene; 2- ethylamino-p-cresol; 2,3-dihydroxynaphthalene; 5-methyl-o-aminophenol; 6-methyl-o-aminophenol; and 2-amino-5-acetaminophenol; 2-methyl-1-naphthol; 1-acetoxy-2-methylnaphthalene; 1,7-dihydroxynaphthalene; resorcinol; 4-chlororesorcinol; 1- 20 naphthol; 1,5-dihydroxynaphthalene; 2,7-dihydroxynaphthalene; 2-methylresorcinol; 1-hydroxy-6-aminonaphthalene- 3-sulfonic acid; thymol (2-isopropyl-5-methylphenol); 1,5-dihydroxy-1,2, 3,4-tetrahydronaphthalene; 2-chlororesorcinol; 2,3-dihydroxy-1,4- naphthoquinone; and 25 1-naphthol-4-sulfonic acid; m-phenylenediamine; 2-(2,4-diaminophenoxy) ethanol; N,N-bis(hydroxyethyl)-m-phenylenediamine; 2,6- diaminotoluene; N,N-bis(hydroxyethyl)-2,4-diaminophenetole; bis(2,4-diaminophenoxy)-1,3-propane; 1-hydroxyethyl-2,4- 30 diaminobenzene; 2-amino- 4 hydroxyethylaminoanisole; aminoethoxy-2,4-diaminobenzene;

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2,4- diaminophenoxyacetic acid; 4,6-bis(hydroxyethoxy)-m-phenylenediamine; 2,4-diamino-5-methylphenetole; 2,4-diamino-5-hydroxyethoxytoluene; 2,4- dimethoxy 1,3-diaminobenzene; and 2,6-bis(hydroxyethylamino) toluene; m-aminophenol; 2-hydroxy-4- carbamoylmethylaminotoluene; m-carbamoylmethylaminophenol; 6- hydroxybenzomorpholine; 2-hydroxy-4-aminotoluene; 2-hydroxy-4-hydroxyethylaminotoluene; 4,6-dichloro-m-aminophenol; 2-methyl-m- aminophenol; 2-chloro-6-methyl-m-aminophenol; 2-hydroxyethoxy-5- aminophenol; 2-chloro-5-trifluoroethylaminophenol; 4-chloro-6-methyl-m- aminophenol; N-cyclopentyl-3-aminophenol; N-hydroxyethyl-4-methoxy-2-methyl-m-aminophenol and 5-amino-4-methoxy-2-methylphenol; 2-dimethylamino-5-aminopyridine; 2,4,5,6-tetra-aminopyrimidine; 4,5-diamino-1-methylpyrazole; 1-phenyl-3-methyl-5-pyrazolone; 6-methoxy-8-aminoquinoline; 2,6-dihydroxy-4-methylpyridine; 5-hydroxy-1,4-benzodioxane; 3,4-methylenedioxyphenol; 4-hydroxyethylamino-1,2-methylenedioxybenzene; 2,6-dihydroxy-3,4-dimethylpyridine; 5-chloro-2,3-dihydroxypyridine; 3,5-diamino-2,6- dimethoxypyridine; 2-hydroxyethylamino-6-methoxy-3-aminopyridine; 3,4- methylenedioxyaniline; 2,6-bis-hydroxyethoxy-3,5-diaminopyridine; 4- hydroxyindole; 3-amino-5-hydroxy-2,6-dimethoxypyridine; 5,6-dihydroxyindole; 7-hydroxyindole; 5-hydroxyindole; 2-bromo-4,5-methylenedioxyphenol; 6-hydroxyindole; 3-amino-2-methylamino-6- methoxypyridine; 2-amino-3-hydroxypyridine; 2,6-diaminopyridine; 5-(3,5-diamino-2-pyridyloxy)-1,3-dihydroxypentane; 3-(3,5-diamino-2-pyridyloxy)- 2-hydroxypropanol and 4-hydroxy-2,5,6-triaminopyrimidine, or combinations thereof.



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**BUFFERING AGENTS**

- 5 The coloring compositions of the present invention which are a mixture of Part A and Part B have a preferred pH in the range of from about 7.5 to about 12, more preferably from about 8 to about 10.
- 10 Buffering agents may be present in part A compositions of the present invention which have a conditioner base, and compositions of the present invention which have a shampoo base. Coloring compositions of the present invention may contain one or more hair swelling agents (HSAs) such as
- 15 urea, to adjust the pH to the desired level. Several different pH modifiers can be used to adjust the pH of the final composition or any constituent part thereof.

- Further examples of suitable buffering agents are ammonium
- 20 hydroxide, urea, ethylamine, dipropylamine, triethylamine and alkanediamines such as 1,3-diaminopropane, anhydrous alkaline alkanolamines such as, mono or di- ethanolamine, preferably those which are completely substituted on the amine group such as dimethylaminoethanol, polyalkylene
- 25 polyamines such as diethylenetriamine or a heterocyclic amine such as morpholine as well as the hydroxides of alkali metals, such as sodium and potassium hydroxide, hydroxides of alkali earth metals, such as magnesium and calcium hydroxide, basic amino acids such as L-alanine, lysine,
- 30 oxylysine and histidine and alkanolamines such as dimethylaminoethanol and aminoalkylpropanediol and mixtures

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thereof. Also suitable for use herein are compounds that form  $\text{HCO}_3^-$  by dissociation in water (hereinafter referred to as 'ion forming compounds'). Examples of suitable ion forming compounds are  $\text{Na}_2\text{CO}_3$ ,  $\text{NaHCO}_3$ ,  $\text{K}_2\text{CO}_3$ ,  $(\text{NH}_4)_2\text{CO}_3$ ,  
5  $\text{NH}_4\text{HCO}_3$ ,  $\text{CaCO}_3$  and  $\text{Ca}(\text{HCO}_3)_2$  and mixtures thereof.

As herein before described certain alkaline buffering agents such as ammonium hydroxide and monoethylamine (MEA) can also act as hair swelling agents (HSA's) such as urea and the  
10 like.

Preferred for use as a buffering agent for the coloring compositions according to the present invention is ammonium hydroxide and/or sodium hydroxide.

15 In oxidizing and coloring kits comprising a portion of peroxide oxidizing agent, which may be present in either solid or liquid form, such as hydrogen peroxide, a buffering agent solution is required to stabilize hydrogen peroxide.  
20 Since hydrogen peroxide is stable in the pH range from 2 to 4, it is necessary to use a buffering agent having a pH within this range. Dilute acids are suitable hydrogen peroxide buffering agents. Phosphoric acid is a preferred agent for buffering hydrogen peroxide solutions.

25 This pH adjustment can be effected by using well known acidifying agents in the field of treating keratinous fibers, and in particular human hair, such as inorganic and organic acids such as hydrochloric acid, tartaric acid,  
30 citric acid, phosphoric acid and carboxylic or sulphonic

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acids such as ascorbic acid, acetic acid, lactic acid, sulphuric acid, formic acid, ammonium sulphate and sodium dihydrogenphosphate/phosphoric acid, disodium hydrogen phosphate/phosphoric acid, potassium chloride/hydrochloric acid, potassium dihydrogen phthalate/hydrochloric acid, sodium citrate/hydrochloric acid, potassium dihydrogen citrate/hydrochloric acid, potassium dihydrogencitrate/citric acid, sodium citrate/citric acid, sodium tartarate/tartaric acid, sodium lactate/lactic acid, sodium acetate/acetic acid, disodium hydrogenphosphate/citric acid and sodium chloride/glycine/hydrochloric acid and mixtures thereof.

#### SOLVENTS

Water is the preferred principal diluent for the compositions according to the present invention. As such, the compositions according to the present invention may include one or more solvents as additional diluent materials. Generally, the solvent is selected to be miscible with water and innocuous to the skin. Solvents suitable for use herein include C<sub>1</sub>-C<sub>20</sub> mono- or polyhydric alcohols and their ethers, glycerine, with monohydric and dihydric alcohols and their ethers preferred. In these compounds, alcoholic residues containing 2 to 10 carbon atoms are preferred. Thus, a particularly preferred group includes ethanol, isopropanol, n-propanol, butanol, propylene glycol, ethylene glycol monoethyl ether, and mixtures thereof.

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These solvents may be present in compositions of the present invention which have a conditioner base, and in compositions of the present invention which have a shampoo base. These solvents may be present in part A compositions of the  
5 invention and part B compositions of the invention.

#### **SURFACTANT MATERIALS**

10 The compositions of the present invention can additionally contain a surfactant system. Suitable surfactants for inclusion in the compositions of the invention generally have a lipophilic chain length of from about 8 to about 22 carbon atoms. Surfactants which are either amphoteric or  
15 anionic or zwitterionic are included in compositions of the present invention which have a shampoo base. In addition, there may be included in shampoo compositions of the present invention, cationic, nonionic or zwitterionic surfactants. Compositions of the invention having a conditioner base can  
20 include cationic, nonionic or zwitterionic surfactants. Surfactants may be present in part A and part B compositions of the invention.

##### **(i) Anionic Surfactants**

25 Anionic surfactants suitable for inclusion in the compositions of the invention include alkyl sulphates, ethoxylated alkylsulphates, alkyl glyceryl ether sulfonates, methyl acyl taurates, fatty acyl glycines, N-acyl  
30 glutamates, acylisethionates, alkyl sulfosuccinates, alkyl ethoxysulphosuccinates, alpha-sulfonated fatty acids, their

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salts and/or their esters, alkyl ethoxy carboxylates, alkyl phosphate esters, ethoxylated alkyl phosphate esters, alkyl sulphates, acylsarcosinates and fatty acid/protein condensates, and mixtures thereof. Alkyl and/or acyl chain  
5 lengths for these surfactants are C12 -C22, preferably C12 - C18 more preferably C12 -C14.

(ii) Nonionic Surfactants

10 The compositions of the invention can also comprise one or more water-soluble nonionic surfactants.

Suitable oil derived nonionic surfactants for use herein include water soluble vegetable and animal-derived  
15 emollients such as triglycerides with a polyethyleneglycol chain inserted; ethoxylated mono and di-glycerides, polyethoxylated lanolins and ethoxylated butter derivatives.

Preferred for use herein are polyethyleneglycol based  
20 polyethoxylated C<sub>9</sub> -C<sub>15</sub> fatty alcohol nonionic surfactants containing an average of from about 5 to about 50 ethyleneoxy moieties per mole of surfactant.

Also suitable for use herein are nonionic surfactants  
25 derived from composite vegetable fats extracted from the fruit of the Shea Tree (*Butyrospermum Karkii* Kotschy) and derivatives thereof. Similarly, ethoxylated derivatives of Mango, Cocoa and Illipe butter may be used in compositions according to the invention. Although these are classified  
30 as ethoxylated nonionic surfactants it is understood that a

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certain proportion may remain as non-ethoxylated vegetable oil or fat.

Other suitable oil-derived nonionic surfactants include  
5 ethoxylated derivatives of almond oil, peanut oil, rice bran  
oil, wheat germ oil, linseed oil, jojoba oil, oil of apricot  
pits, walnuts, palm nuts, pistachio nuts, sesame seeds,  
rapeseed, cade oil, corn oil, peach pit oil, poppyseed oil,  
pine oil, castor oil, soybean oil, avocado oil, safflower  
10 oil, coconut oil, hazelnut oil, olive oil, grapeseed oil,  
and sunflower seed oil.

(iii) Amphoteric Surfactants

15 Amphoteric surfactants suitable for use in the compositions  
of the invention include: alkyl betaines, alkyl sultaines,  
alkyl amphoacetates, alkyl amphodiacetates,  
alkyl amphopropionates, and alkyl amphodipropionates.

20 (iv) Zwitterionic Surfactants

Water-soluble auxiliary zwitterionic surfactants suitable  
for inclusion in the compositions of the present invention  
include alkyl betaines.

25

Water-soluble auxiliary sultaine surfactants suitable for  
inclusion in the compositions of the present invention  
include alkyl sultaines. Preferred for use herein is coco  
amido propylhydroxy sultaine.

30

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Water-soluble auxiliary amine oxide surfactants suitable for inclusion in the compositions of the present invention include alkyl amine oxide corresponding to the general formula  $R_1R_2R_3NO$ , wherein  $R_1$  contains an alkyl, alkenyl or monohydroxyl alkyl radical of from about 8 to about 18 carbon atoms, from 0 to about 10 ethylene oxide moieties, and from 0 to about 1 glyceryl moiety, and  $R_2$  and  $R_3$  contain from about 1 to about 3 carbon atoms and from 0 to about 1 hydroxy group, e.g., methyl, ethyl, propyl, hydroxyethyl, or hydroxypropyl radicals.. Preferred amine oxides include cocoamidopropylamine oxide, lauryl dimethyl amine oxide and myristyl dimethyl amine oxide.

(v) Cationic Surfactants

Cationic surfactants include polyethylene condensates of alkyl phenols, condensation products of ethylene oxide, propylene oxide, and ethylene oxide, propylene oxide, and ethylene diamine, long chain tertiary amine oxides, long chain tertiary phosphine oxides, and the like.

Conditioners

The conditioning compositions of this invention also contain at least a water-soluble or water-dispersible quaternary nitrogen-containing conditioning agent that is also sometimes referred to herein as a cationic compound. A long chain fatty alcohol is also present in more preferred compositions, and a tertiary amidoamine is additionally present in particularly preferred compositions.

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The quaternary nitrogen-containing conditioning agents are preferably present at from about 0.5 to about 5 percent by weight of the composition as an active ingredient. More preferably, the quaternary nitrogen-containing conditioning agent is present at from about 2 to about 3 weight percent, as an active ingredient.

The class of quaternary nitrogen-containing conditioning agents useful herein contain one quaternary nitrogen atom having (a) two long aliphatic chains and (b) two identical or different short chain alkyl groups having one or two carbon atoms, each bonded to the quaternary nitrogen atom. The two long chains each contain about 12 to about 18 carbon atoms.

Illustrative conditioning agents include distearyldimethylammonium chloride and dilauryldimethylammonium chloride. These compounds are named Quaternium-5 and Quaternium-47, respectively, in the CTFA Cosmetic Ingredient Dictionary, 2nd ed., 1977, published by the Cosmetic, Toiletry and Fragrance Association, Inc., hereinafter referred to as the CTFA Dictionary.

It is noted that the long aliphatic chain of the before-mentioned conditioning agents need not be solely or primarily of one chain length, i.e., the long chain need not be cetyl, myristyl, lauryl or stearyl. Rather, conditioning agents whose long aliphatic chain contains a mixture of lengths can be used. Such conditioning agents are conveniently prepared from naturally occurring materials,



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such as tallow, coconut oil, soya oil and the like, or from synthetically produced mixtures. Examples of useful conditioning agents having mixed aliphatic chain lengths include dimethyldi-(hydrogenated tallow)ammonium chloride and dialkyldimethylammonium chloride wherein each alkyl group is a saturated group consisting primarily of 16 carbon atoms. These quaternary nitrogen-containing conditioning agents are named Quaternium- 18 and Quaternium-31, respectively, in the CTFA Dictionary.

10

The compositions of this invention can also be in the form of emulsions that contain additional amounts of hydrophilic and/or hydrophobic ingredients. Emulsions containing additional hydrophobic materials are particularly preferred. It is preferred that those emulsions be stable to phase separation at a temperature of about 25 degree C for a period of about 24 hours after their preparation. The emulsions are more preferably stable to phase separation at temperatures normally found in commercial product storage and shipping for periods of one year or more.

20

### THICKENERS

Thickeners may be included in compositions of the invention which have a shampoo base, and compositions of the invention which have a conditioner base, and thickeners may be included in part A and part B compositions of the invention. Long chain fatty alcohols having from about 11 to about 18 carbon atoms in the long fatty chain can be thickener constituents of the conditioning emulsions of this invention. These alcohols can be used alone, or in

30

- 25 -

admixture with each other. When included in the compositions, the alcohol is preferably present at from about 0.5 to about 10 weight percent of the composition, and more preferably at from about 2 to about 5 weight percent.

5

Lauryl alcohol, oleyl alcohol, myristyl alcohol, stearyl alcohol, and the like, and mixtures thereof are contemplated herein. In addition, mixtures of natural or synthetic fatty alcohols having fatty chain lengths of from about 11 to about 18 carbons are also useful. Several such mixtures are available commercially, and are exemplified by the material containing a mixture of synthetic alcohols with 12 to 15 carbons in the alkyl chain sold under the trademark NEODOL 25 by Shell Chemical Company, and the material containing a mixture of synthetic alcohols with chain lengths of 12 to 16 carbons sold under the trademark ALFOL 1216 Alcohol by Conoco Chemicals.

Thickening agents suitable for use in the compositions herein may also be selected from oleic acid, cetyl alcohol, oleyl alcohol, sodium chloride, cetearyl alcohol, stearyl alcohol, synthetic thickeners such as Carbopol, Aculyn and Acrosyl and mixtures thereof. Preferred thickeners for use herein are Aculyn 22 (RTM), steareth-20 methacrylate copolymer; Aculyn 44 (RTM) polyurethane resin and Acusol 830 (RTM), acrylates copolymer that are available from Rohm and Haas, Philadelphia, Pa., USA. Additional thickening agents suitable for use herein include sodium alginate or gum arabic, or cellulose derivatives, such as methyl cellulose or the sodium salt of carboxymethylcellulose or acrylic polymers.

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Fatty alcohols of the above discussed carbon chain lengths which are ethoxylated to contain an average of one or two moles of ethylene oxide per mole of fatty alcohol can be used in place of the fatty alcohols themselves. Examples of such useful ethoxylated fatty acids include ethylene glycol cetyl ether, polyoxyethylene (2) stearyl ether, and the like; the exemplary compounds having CTFA Dictionary names of Ceteth-1 and Steareth-2, respectively.

#### OPTIONAL INGREDIENTS

The compositions of the present invention can comprise a wide range of optional ingredients. Examples of these functional classes include: anticaking agents, antioxidants, binders, biological additives, bulking agents, chelating agents, chemical additives, colorants, cosmetic astringents, cosmetic biocides, denaturants, drug astringents, emulsifiers, film formers, fragrance components, humectants, opacifying agents, plasticizers, preservatives, propellants, reducing agents, solvents, foam boosters, hydrotropes, solubilizing agents, suspending agents (nonsurfactant), sunscreen agents, ultraviolet light absorbers, and viscosity increasing agents (aqueous and nonaqueous). Examples of other functional classes of materials useful herein that are well known to one of ordinary skill in the art include solubilizing agents, sequestrants, and the like.

Other optional ingredients include organic acids. A non-exclusive list of examples of organic acids which can be

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used as the proton donating agent are adipic acid, tartaric acid, citric acid, maleic acid, malic acid, succinic acid, glycolic acid, glutaric acid, benzoic acid, malonic acid, salicylic acid, gluconic acid, polyacrylic acid, their  
5 salts, and mixtures thereof. Non-exclusive lists of examples of mineral acid for use herein are hydrochloric, phosphoric, sulfuric and mixtures thereof.

We have found by experimentation that daily hair care  
10 products can achieve durable desired hair color. As noted above, the daily hair care product consists of two parts.

Part A: Dye intermediates in a conditioner or shampoo base at alkaline pH  
15 Part B: Hydrogen peroxide in a conditioner or shampoo base at acidic pH

Part A is mixed with part B and applied to hair. The reason current hair coloring products come in two packages is  
20 because the mixture of the coloring component and the oxidizing component is unstable and the two components must be kept apart until just before use. Similarly part A and part B of the present invention must be kept apart until just before use. By varying the concentration of the  
25 actives and the treatment time, the amount of color on hair could be varied while minimizing hair damage. To make the product more convenient and fool proof, part A and B can be packaged in dual dispensing systems where both parts are mixed out side of the package when dispensed which is then  
30 applied to the wet hair as a conditioner or shampoo.

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Depending upon the amount of color desired, the treatment time could be varied from two minutes or longer.

Such conditioner or shampoo treatments would add color to hair gradually without damage due to lower contact time. Each subsequent treatment would add color until the desired shade is obtained. Depending upon the concentration of the actives and contact time, a desired shade may be reached in six to eight treatments. We have found that since any one treatment does not exceed the threshold of irreversible damage, the total damage resulting from multiple treatments is lower than the damage from a single conventional treatment. Such a process gives the user control on the amount of color deposited on her hair, and also the option to discontinue further applications if the color delivered is not to her liking. She also has the option to switch to another color shade immediately without having to wait the six to eight weeks that is recommended for conventional treatments. With conventional hair color treatment, it is not recommended to perm and color hair simultaneously due to extensive damage. However, since this method colors the hair with minimum damage, perming can be done in the same time frame with this progressive coloring treatment.

## **METHOD FOR USING COMPOSITIONS OF THE INVENTION**

Shampoo the hair as usual. Pump the composition of the invention into the palm and mix. Apply product to the hair like a regular conditioner. Rinse the hands. Leave product in the hair for about 2 minutes for color maintenance to

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about 5 minutes for color change. Rinse the hair thoroughly.

The following examples, which were made, are shown as  
5 illustrations only and are not intended to limit the scope  
of the invention.

Unless indicated otherwise, all parts and percentages used  
in the examples are parts and percentages by weight of  
10 active material based on the weight of the respective  
composition.

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**EXAMPLE #1**

Dark Brown Color conditioner: Part A

5		
	1. DI Water	70.00
	2. Stearamidopropyl dimethylamine	0.50
	3. Dicetyldimonium chloride/PG, 68%/27% active	2.10
	4. Stearyl alcohol and Ceteareth-20, 70% active	1.00
10	5. Cetyl alcohol	3.60
	6. DI water	3.00
	7. Disodium EDTA	0.10
	8. Dimethicone 100%	1.00
	9. DC silicone fluid 245	1.80
15	10. Preservatives	0.18
	11. DMDM Hydantoin 55% active	0.10
	12. Fragrance	0.20
	13. Sodium metabisulfite	0.10
	14. DI water	15.11
20	15. m- Aminophenol	0.03
	16. N,N Bis(2-hydroxyethyl)-p-phenylenediamine sulfate	0.13
	17. p-Phenylenediamine	0.45
	18. o-Aminophenol	0.05
	19. Resorcinol	0.25
25	20. Sodium hydroxide 50% solution	0.40

PH= 8 to 9

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## Manufacturing Process:

- Weigh the ingredients(item#15 to 19) needed into an  
5 appropriate container;  
Flush the container(tank) with nitrogen gas;  
Add item #1 into a suitable container. Heat to 82-85°C (180-  
185F). Keep the Nitrogen blanket;  
Add pre-weighed dyes with moderate agitation. Keep the  
10 Nitrogen blanket;  
Add item #3 with moderate agitation;  
Add item #2, 4 and 5, dissolve completely;  
Mix batch at approximately 82-85°C (180-185F) for at least an  
hour with agitation until particles; are completely  
15 dissolved. Check for the particles;  
Begin cooling. Keep the nitrogen blanket with moderate  
agitation;  
Prepare EDTA and sodium phosphate solution using item#6 DI  
water;  
20 At 54°C (130F) add the EDTA solution to the batch;  
At 43°C (110F) or below, add items # 8, 9,10,11,12,13; mix  
well;  
Adjust the pH to around 10.0 using item # 20; keep the  
Nitrogen blanket through entire process;  
25 Qs with DI water item # 14.



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## Peroxide conditioner: Part B

	1. D.I. Water	74.00
5	2. Liquid Citric acid, 50%	0.20
	3. Stearamidopropyl dimethylamine	0.50
	4. Dicetyldimonium chloride/PG, 68%/27%	2.10
	5. Stearyl alcohol and Ceteareth-20, 70%	1.00
	6. Cetyl alcohol	3.80
10	7. DI water	5.00
	8. Disodium EDTA	0.10
	9. Dimethicone 100%	1.00
	10. DC silicone fluid 245	1.80
	11. Hydrogen Peroxide(35%)	10.00
15	12. DMDM Hydantoin 55%	0.10
	13. Fragrance A42867H/7454965	0.20
	14. Phosphoric acid, 85%	0.09

PH=2.5 to 3.5

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## MANUFACTURING PROCESS:

1. Add item#1 into a suitable container. Heat to 82-85°C (180-185F)
2. Add item#2 with moderate agitation
3. Add item#4, dissolve completely
4. At 74-77°C (165-170F), add item#3,5,6
5. Mix batch at approximately 82-85°C (180-185F) for at least an hour with agitation until particles are completely dissolved. Check for the particles
6. Begin cooling.
7. In a separate container dissolve item#8 in item#7
8. At 54°C (130F) add the EDTA solution to the batch.
9. At 43°C (110F) or below, add item# 9, 10, 11, 12, and 13  
Mix well
10. Adjust the pH with item#14 to 2.7 to 3.0
11. Qs with water

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## METHOD OF USING ABOVE CONDITIONERS:

Shampoo the hair tresses. Take equal part of color  
5 conditioner of part A and B (formula#1), mix and apply to  
the wet hair tresses, keep for two minutes, and rinse well.  
Repeat the above procedure for subsequent treatment.  
Collect the hair tress after 2, 4 and 6 treatments. Measure  
the change in color delta E using McBeth ColorEye.

10

The table below summarized the part A formulation for  
various shades. One can use same peroxide conditioner part  
B for all shades.

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Ingredients	Hair Color Conditioner: Part A					
	Dark	Light	Dark	Light	Dark	Light
	Brown	Brown	Blonde	Blonde	Auburn	Auburn
Composition No.	65	66	67	68	69	71
Deionized water	70.00	70.00	70.00	70.00	70.00	70.00
Stearamidopropyl dimethylamine	0.50	0.50	0.50	0.50	0.50	0.50
Dicetyldimonium chloride	2.10	2.10	2.10	2.10	2.10	2.10
Stearyl alcohol and Ceteareth-20	1.00	1.00	1.00	1.00	1.00	1.00
Cetyl alcohol	3.60	3.60	3.60	3.60	3.60	3.60
Disodium EDTA	0.10	0.10	0.10	0.10	0.10	0.10
Sodium phosphate	-	0.20	0.20	0.20	-	0.20
Deionized water	18.41	18.65	19.32	15.00	17.99	15.00
Fragrance	0.20	0.20	0.20	0.20	0.20	0.20
Dimethicone	0.10	0.10	0.10	0.10	0.10	0.10
Cyclopentasiloxane	1.80	1.80	1.80	1.80	1.80	1.80
Preservatives	0.18	0.18	0.18	0.18	0.18	0.18
Sodium metabisulfite	0.15	0.15	0.15	0.15	0.15	0.15
4-amino-2-hydroxytoluene (p-amino-o-cresol) PAOC	-	-	-	-	0.70	0.70
m-aminophenol: Rodol EG	0.03	-	-	-	-	-
o-aminophenol: Rodol 2G	0.05	0.01	0.05	0.03	0.20	0.10
p-aminophenol: Rodol P base	-	-	0.05	0.03	0.20	0.30
N,N Bis(2-hydroxyethyl)-p-phenylenediamine	0.13	-	-	-	-	-

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sulfate:HED						
2-methylresorcinol: RodolMRP	-	-	-	-	-	-
1-Napthol:Rodol ERN	-	-	-	-	-	-
p-phenylenediamine:R odol D type J	0.70	0.35	0.02	0.01	0.15	0.03
Resorcinol:Rodol RS	0.35	0.45	0.03	0.01	0.03	0.03
Phenyl methyl pyrozolone (Rodol PMP	-	0.01	-	-	-	-
HC Red#3	-	-		-	0.20	0.02
Sodium hydroxide, liquid 50% active	0.4-0.6	0.4-0.6	0.4-0.6	0.4-0.6	0.4-0.6	0.4-0.6
Mixed pH=	7.5-8.0	9.0-9.5	9.0-9.5	9.0-9.5	8.0-8.5	9.0-9.5

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**EXAMPLE # 2**

L'Oreal Dark Brown permanent hair color

5

Color the hair tresses using L'Oreal dark brown permanent hair color. Follow the instruction sheet. Measure the change in color delta E using McBeth ColorEye.

- 10 The changes in Delta E values are summarized in below table. You can see from the results that change in color after one 30-min. treatment with L'Oreal Dark Brown is very similar to six- 2-min. treatment of color conditioner. The good correlation was observed with number of treatment and change
- 15 in the color of the hair. It takes six treatments to achieve a single 30 minutes treatment of permanent color.

L'Oreal's Preference: Invention: Dark Brown

Dark Brown: Delta E      Delta E

1 treatment -30 min.	4.19	
2 treatments-2 min. each		1.68
4 treatments-2 min. each		3.45
6 treatments-2 min. each		4.02

- 20 It can be seen that six treatments of two minutes per each treatment with the dark brown color composition of the present invention, resulted in approximately the same color change, Delta E, as one thirty minute treatment with L'Oreal's dark brown color composition.

25

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## EXAMPLE #3

The combing experiment was carried out to evaluate the extent of damage. Wet combing evaluation technique has been  
5 used to correlate damage. Lower wet combing force indicates less damage. The above tresses were evaluated via Instron to measure combing force.

Results indicated that the tresses treated with L'Oreal dark  
10 brown required much higher combing force than tresses treated with color conditioner.

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## EXPERIMENTAL

To evaluate the wet combing performance of a Dark Brown and  
5 Light Brown Color Conditioner of the invention the  
measurements below were made. The combing force of hair  
treated 30 times with Light Brown composition was measured  
and compared with combing force of hair treated with one  
treatment of L'Oreal Preference. Also, tensile strength  
10 damage caused by the composition of the invention was  
compared to tensile strength damage caused by a commercial  
color product (Preference by L'Oreal). Wet combing  
experiments have been carried out on the Instron 5500  
series. All testing was carried out by applying 0.3 mL of  
15 product to bleached and waved 2g hair tresses. Results are  
expressed in terms of the maximum load (highest force  
encountered during combing) and combing energy (area under  
the combing curve). Finesse extra moisturizer and Extra  
body have also been included in this study as internal  
20 controls. Wet combing results are given below.



- 40 -

Statistical analysis is presented in terms of the Tukey HSD test and the less rigorous LSD test.

# 5 Multiple Range Tests for M\_Ld by Treatment

Method: 95.0 percent Tukey HSD

Treatment	Count	Mean	Homogeneous Groups
Comp. No. 23	8	9.14	X Comp. No. 23, Dark brown
Fin_M	8	9.645	X Finesse Moisturizing
Fin_B	8	13.5813	X Finesse Bodifying

15

# Multiple Range Tests for M\_Ld by Treatment

Method: 95.0 percent LSD

Treatment	Count	Mean	Homogeneous Groups
Comp. No. 23	8	9.14	X Comp. No. 23, Dark brown
Fin_M	8	9.645	X Finesse Moisturizing
Fin_B	8	13.5813	X Finesse Bodifying

25

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## Multiple Range Tests for T\_Energy by Treatment

5 Method: 95.0 percent Tukey HSD

Treatment		Count	Mean		Homogeneous Groups
Comp. No. 23		8	8.40875	X	Comp. No. 23, Dark brown
Fin_M		8	9.35875	X	Finesse Moisturizing
10	Fin_B	8	12.4	X	Finesse Bodifying

## Multiple Range Tests for T\_Energy by Treatment

15 Method: 95.0 percent LSD

Treatment		Count	Mean		Homogeneous Groups
3Comp. No. 23		8	8.40875	X	Comp. No. 23, Dark brown
Fin_M		8	9.35875	X	Finesse Moisturizing
20	Fin_B	8	12.4	X	Finesse Bodifying

The above data indicate that the combing force of Dark brown composition is very similar to the standard Finesse moisturizing conditioner. Higher combing force indicates difficult to comb.

Statistical analysis is presented in terms of the Tukey HSD test and the less rigorous LSD test.

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## Multiple Range Tests for Max\_Ld by Treatment

5 Method: 95.0 percent Tukey HSD

Treatm	Count	Mean		Homogeneous Groups
Untreated	8	19.4125	X	Untreated
Rainbow 30x	8	19.7013	X	Invention Light Brown
				Conditioner 30x
L'Oreal	8	53.4988	X	L'Oreal Preference

10

## Multiple Range Tests for Max\_Ld by Treatment

15 -----

Method: 95.0 percent LSD

Treatment	Count	Mean		Homogeneous Groups
Untreated	8	19.4125	X	Untreated
Invention 30x	8	19.7013	X	Invention Light Brown
				Conditioner 30x
L'Oreal	8	53.4988	X	L'Oreal Preference

20

25 The above data indicate that the combing force of hair treated 30 times with Light brown composition is very similar to the untreated hair tresses. However, the combing force of hair treated with one treatment of L'Oreal is much higher than hair treated with Light Brown compositions. Again, as mentioned, higher combing force indicates

30 difficult to comb and higher damage.

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## TENSILE TESTING

5 All tensile testing has been carried out on the Diastron  
MTT600. The tensile strength of approx. 50 individual  
fibers were measured for each treatment. The diameter of  
these individual fibers is measured prior to testing to  
allow the force to be normalized against cross sectional  
area.

10

That is:  $\text{Stress} = \text{Force} / \text{Cross sectional area}$

The tensile properties of hair may be taken to reflect the  
extent of structural integrity. Various measurements may be  
15 used to assess these tensile properties. Common parameters  
include the stress at break, work to break or extension to  
break. The complex structural properties of hair dictate  
that the wet and dry tensile properties reflect the  
properties of different regions. Wet tensile properties may  
20 be regarded as being representative of the alpha helical  
keratin protein within the hair's microfibrils; while the  
dry tensile properties also includes a substantial  
contribution from the intercellular cement. Many previous  
sets of results have shown that changes in tensile  
25 properties as a function of a treatment are more often seen  
when considering the wet tensile properties. For this  
reason, these experiments represent measurement of the wet  
tensile properties of the various hair treatments.

30 Each set of crimped hair samples was soaked in water for 30  
mins prior to testing. In addition, the slots in the

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tensile testing carousel were filled with water to ensure that the fibers remained soaked for the progression of the experiment. All tress treatments were carried out by the requester.

5

Break stress results are shown below.

Statistical analysis is again presented in terms of the Tukey HSD test and the less rigorous LSD test.

10

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## Multiple Range Tests for B\_STRESS by TREATMENT

5 Method: 95.0 percent Tukey HSD · Break Stress

(gm force/micron<sup>2</sup>)

	TREATMENT	Count	Mean	Homogeneous Groups	
10	L`OREAL	45	0.0170723	X	L`Oreal
					Preference, Dark Brown
	UNTREAT	45	0.0182494	X	Untreated
	Comp. No. 23	40	0.0185977	X	3030-23 Invention - Dark Brown

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## Multiple Range Tests for B\_STRESS by TREATMENT

---

Method: 95.0 percent LSD      Break Stress (gm force/micron<sup>2</sup>)

5	TREATMENT	Count	Mean		Homogeneous Groups
	L'OREAL	45	0.0170723	X	L'Oreal Preference, Dark Brown
	UNTREAT	45	0.0182494	X	Untreated
10	Comp. No. 23	40	0.0185977	X	Comp. No. 23 Dark Brown

---

The above results would seem to be suggesting that the chemical treatment L'Oreal Preference color has lowered the break stress, while the conditioner of the invention has had no effect on this tensile parameter remains as untreated. It indicates that hair treated with L'Oreal preference is easier to break compare to the untreated hair and the hair treated with conditioner of the invention.

20

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The following is the example of formulation of Dark brown Coloring Shampoo:

## Part A

5	Item	Ingredients	Dark
			Brown
	1	Deionized water	60.00
10	2	Polymer JR	0.30
	3	Cocamidopropyl betaine	7.00
	4	SCAP	25.00
	5	DC-1870 HV	0.08
	6	Propylene glycol	0.30
15	7	Versene 100	0.20
	8	Fragrance	0.20
	9	Kathon CG(1.5% active)	0.08
	10	DMDM hydantoin	0.10
	11	Sodium metabisulfite	0.15
20	12	m-aminophenol:Rodol EG	0.03
	13	o-aminophenol:Rodol 2G	0.05
	14	N,N Bis(2-hydroxyethyl)-p-phenylenediamine sulfate:HED	0.13
	15	p-phenylenediamine:Rodol D type J	0.70
25	16	Resorcinol:Rodol RS	0.35
	17	Sodium hydroxide, liquid 50% active	0.4-0.6

pH= 7.5-8.0

Viscosity= 3000 to 6000cps (spindle#4, 20 rpm)



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## Manufacturing Process:

- Weigh the ingredients (item#11 to 16) needed into an  
5 appropriate container  
Flush the container (tank) with nitrogen gas  
Add item#1 into a suitable container. Heat to 82-85°C (180-  
185F), Keep the Nitrogen blanket  
Add pre-weighed dyes with moderate agitation. Keep the  
10 Nitrogen blanket  
Add item#2 with moderate agitation  
Add item#3, and 4 dissolve completely  
Mix batch at approximately 82-85°C (180-185F) for at least an  
hour with agitation until particles are completely  
15 dissolved. Check for the particles  
Begin cooling. Keep the nitrogen blanket with moderate  
agitation.  
At 54°C (130F) add the Versene solution to the batch.  
At 43°C (110F) or below, add item# 5,6,8,9,10, Mix well  
20 Adjust the pH with item#17 to around 10.0 Keep the Nitrogen  
blanket through entire process  
Qs with DI water

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## Part B: Peroxide Shampoo

Item#	Chemical Name	Actual Weight%
1	D.I. Water	39.00
2	Polymer JR 30M	0.30
3	Sodium C14-C16 Olefin Sulfonate	35.00
4	Lauramine oxide 29%	3.70
5	Lauryl alcohol	0.50
6	DC-1870 HV	1.60
7	DI water	9.00
8	DMDM Hydantoin 55%	0.10
9	Hydrogen peroxide, 35%	10.00
10	Fragrance	0.20
11	Phosphoric acid, 85%	0.60

## Specification:

pH= 2.7 to 3.0

Viscosity= 3000 to 6000cps(spindle#4, 20 rpm)

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## Manufacturing Process:

1. Add item#1 into a suitable container. Heat to 82-85°C (180-185F)
2. Add item#2 with moderate agitation
3. At 74-77°C (165-170F), add item#3,4,5,
4. Mix batch at approximately 71-77°C (160-165F) for at least an hour with agitation until particles are completely dissolved. Check for the particles
5. Begin cooling.
6. At 43°C (110F) or below, add item# 6,7,8,9,10 Mix well
7. Adjust the pH with item#11 to 2.7 to 3.0
8. Qs with water

Without wishing to be bound by theory, it is believed that  
10 the following mathematical formulae schematically describe  
the color change results and the hair damage results, which  
are obtained through the use of the compositions and methods  
of the present invention.

20 Hair damage = (pH + concentration of oxidizing agent)  
times the contact time; with the proviso that when the  
contact time is about two minutes or less, then there is no  
appreciable hair damage no matter how high the number of  
25 treatments.

Thus, if the contact time is kept at about two minutes or below for each treatment with compositions of the invention then there is no appreciable hair damage no matter how many color application treatments according to the invention are performed.

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## EXAMPLE #9

## Light Brown Color conditioner: Part A

5		
	1. DI Water	70.00
	2. Stearamidopropyl dimethylamine	0.50
	3. Dicetyldimonium chloride/PG, 68%/27%	2.10
	4. Stearyl alcohol and Ceteareth-20, 70%	1.00
10	5. Cetyl alcohol	3.60
	6. DI water	3.00
	7. Disodium EDTA	0.10
	8. Dimethicone 100%	1.00
	9. DC silicone fluid 245	1.80
15	10. Kathon CG 1.5%	0.08
	11. DMDM Hydantoin 55%	0.10
	12. Fragrance A42867H/7454965	0.20
	13. Sodium metabisulfite	0.10
	14. DI water	15.11
20	15. p-Phenylenediamine	0.35
	16. o-Aminophenol	0.01
	17. Resorcinol	0.45
	18. Phenyl methyl pyrozolone	0.01
	19. Sodium hydroxide 50%	0.40

25

PH= 8 to 9

## Light Brown Color conditioner: Part B.

30	1. D.I. Water.	74.00
	2. Liquid Citric acid, 50%	0.20

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	3. Stearamidopropyl dimethylamine	0.50
	4. Dicetyldimonium chloride/PG, 68%/27%	2.10
	5. Stearyl alcohol and Ceteareth-20, 70%	1.00
	6. Cetyl alcohol	3.80
5	7. DI water	5.00
	8. Disodium EDTA	0.10
	9. Dimethicone 100%	1.00
	10. DC silicone fluid 245	1.80
	11. Hydrogen Peroxide(35%)	10.00
10	12. DMDM Hydantoin 55%	0.10
	13. Fragrance	0.20
	14. Phosphoric acid, 85%	0.09

PH=3.0

15

Take equal part of color conditioner of part A and B  
(formula#1), mix and apply to the hair tresses, keep for 30  
minutes, and rinse well. Measure the change in color delta E  
20 using McBeth ColorEye.

EXAMPLE #10

Part A:25 Light Brown using conventional color base:

	1. Laureth-4	12.40
	2. Neodol 23	19.10
	3. Oleth-10	28.90
30	4. Hexylene glycol	13.00
	5. Hamp-ene-acid	0.10

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	6. Isoascorbic acid	0.10
	7. Fragrance	0.20
	8. Sodium metabisulfite	0.10
	9. p-Phenylenediamine	0.35
5	10. o-Aminophenol	0.01
	11. Resorcinol	0.45
	12. Phenyl methyl pyrozolone	0.01
	13. Sodium hydroxide 50%	0.40
	14. DI water	

10

PH<sub>7</sub> 8 to 9

## Part B:

## Peroxide solution:

15	1. D I water	78.00
	2. Hydrogen peroxide 35%	18.0
	3. Polysorbate-20	1.0
	4. Polyquate-6	1.0

20 PH= 3.0

Method of using above Hair coloring products:

Experiment

25 Gradual color delivery

Shampoo the blonde hair tresses. Take equal parts of color conditioner of part A and B , mix and apply to the wet hair tresses, keep for two minutes, and rinse well. Repeat

30 the above procedure for subsequent treatment. Collect the

- 55 -

hair tress after 2, 4 and 8 treatments. Measure the change in color delta E using McBeth ColorEye.

Similarly, shampoo the blonde hair tresses. Take equal  
 5 part of color conditioner of part A and B (formula#2), mix  
 and apply to the wet hair tresses, keep for two minutes, and  
 rinse well. Repeat the above procedure for subsequent  
 treatment. Collect the hair tress after 2, 4 and 8  
 treatments. Measure the change in color delta E using McBeth  
 10 ColorEye.

	Conventional	Invention: Light
	Hair color: Light	Brown
	Brown: Delta E	Delta E
2 treatments-2 min. each	20.02	29.1
4 treatments-2 min. each	24.27	34.68
8 treatments-2 min. each	31.18	44.55

The above results indicate that a composition of the new invention can deposit 30% more color than a conventional hair color composition.

#### 15 Treatment product

The new composition can be used as a treatment product also. The result of the following experiment suggests that the new



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conditioner base deposits about 30% more color than conventional surfactant base. Along with this, the new base gives very little damage compared to a conventional base. A post treatment conditioner is therefore not needed. However,  
 5 with a conventional base, one would need post treatment conditioner.

Take equal amounts of color conditioner of part A and B (formula #1), mix and apply to the hair tresses, leave on  
 10 the hair tresses for 30 minutes, and rinse well. Measure the change in color delta E using McBeth ColorEye.

The changes in delta E values are summarized in the table below. It can be seen from the results that the change in  
 15 color after one 30-minute treatment with the base of the invention is about 30% higher than color developed by a conventional base.

	Conventional color base:	New invention base Light Brown Delta
	Light brown Delta E	E
1X-30 mins.	33.085	44.485

20

Treatment of hair with compositions of the invention as described herein gives said hair good attributes such as lower wet combing force, higher break stress, lower amounts of cysteic acid (which are an indicator of hair damage),

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good hair color change, less color fading, less damage to hair, and more intense color to hair as described just below. Also described below is a method for applying a composition of the invention at set time intervals so as to  
5 avoid root outgrowth and reduce color fading

#### Combing index-

10 The combing experiment has been carried out to evaluate the extent of damage. Wet combing evaluation technique has been used to correlate damage. The combing index was measured to evaluate the extent of damage. Higher index (more than one) number indicates lower damage.

15

Combing index = Combing force of untreated hair/ combing force of treated with color shampoo

20 The above tresses were evaluated via Instron to measure combing force.

Treatments	Combing force
25 Untreated hair	26.15
Treated with color conditioner	9.25

Combing index = Combing force of untreated hair/ combing  
30 force of treated with color shampoo

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$$= 26.15/9.25$$

$$= 2.82$$

5 Wet combing force:

After conventional hair color treatment, it is hard to comb the hair. Harder combing indicates more hair damage. The combing force was measured using an Instron tester.

10

The combing force with new conditioner composition is preferably in the range of 5 to 55 gmforce, more preferably 5 to 20 and even more preferably 5 to 10 gmforce.

15

Break stress:

20

After conventional hair color treatment, the hair becomes weak and easy to break. The weak hair is again a sign of damage. The strength of the hair was measured using an Instron.

25

The break stress with a conditioner composition of the invention would preferably be in the range of 0.005 to 0.03 gmforce/micron, more preferably 0.005 to 0.025, and even more preferably 0.005 to 0.018 gmforce/micron.

30

Cysteic acid:

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Much of the hair damage associated with conventional hair color treatment comes from the oxidation of cystine residues to the corresponding cysteic acid, with a consequent decrease in the tensile strength of hair as these cross-  
 5 linkages are destroyed. A good measure of oxidative damage is thus the amount of cysteic acid formed in hair.

Infrared transmission spectroscopy has been used to determine cysteic acid content in hair. The ratio of  
 10 absorption at  $1040\text{ cm}^{-1}$  /absorption at  $1240\text{ cm}^{-1}$  would indicate the extent of damage. Lower the ratio indicates less hair damage.

The ratio of 1040/1240 with new color compositions would  
 15 preferably be in the range of 0.01 to 1.5, more preferably 0.01 to 1.0, and even more preferably 0.01 to 0.5

Total hair damage:

20 Hair damage done by hair coloring compositions can be calculated, schematically, according to the following mathematical formulae:

25 % Damage = Chemical damage X Physical damage

% Damage = amount of cysteic acid X combing force<sub>cm</sub> X  
 breaking stress

force<sub>cm</sub>/micron<sup>2</sup> X 100

30 % Damage using L'Oreal's conventional preference permanent hair color for example =

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$$0.75 \times 48 \times 0.02 \times 100$$
$$= 72 \% \text{ damage}$$

5    % Damage using new hair color composition:

$$0.25 \times 20 \times 0.015 \times 100$$

$$= 7.5\% \text{ damage}$$

10

The above numbers indicate that the hair color compositions of the invention damage the hair to a much lower extent than conventional permanent hair color. The invention relates to a method for adding color to hair which involves causing  
15    about 5 to about 10% damage to said hair per week, based on the above formulae and depending on the frequency of use.

Color change/color control:

20    The conventional permanent hair color system gives the color change delta E of 5 to 65 on blonde hair, and color change up to delta E of 1 to 8 on brown hair with one treatment. In conventional hair coloring treatments, consumers have little or no control of color, control of hue and control of  
25    lightening.

With the composition of the invention and its method, there can be delivered delta E of 0.1 to 65 on blonde hair and delta E of 0.1 to 8 on brown hair.

30

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When a dark brown color composition of the present invention is applied to dark brown hair, then after one application there can be a delta E from about 0.1 to about 0.2.

- 5 When a dark brown color composition of the present invention is applied to virgin blonde hair, then after one application there can be a delta E from about 10 to about 30.

When a dark brown color composition of the present invention  
10 is applied to bleached blonde hair, then after one application there can be a delta E from about 20 to about 40.

- 15 Root outgrowth:

A conventional permanent hair color system is used once in 4 to 6 weeks. During this time due to the new hair growth, roots look totally different than rest of the hair. On  
20 average the hair grows 1 cm /month or 0.3 mm/day.

With the present compositions and methods, using said compositions as conditioners, one would add color on each application of said compositions. Laboratory evaluation  
25 indicates that one would add 10 % of the color change per conditioning treatment.

The amount of color added is determined by the following mathematical formulae.

30

The length of the new hair = 0.3 mm X no. of days

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% color added to new hair (10days) = No of days X % color  
added per day  
= 10 X 10% = 100% color

5

Due to the constant addition of the color 10% per day, one will not be able to see root outgrowth.

The invention relates to a method for adding color to hair  
10 which involves adding to said hair about 5 to about 10%,  
preferably about 4 to about 8% color per day, based on the  
above formulae and depending on the frequency of use.

15 Color fading:

A conventional permanent hair color system is used once in 4  
to 6 weeks. During this time color fades with washing, and  
outside exposure due to the weathering effect. The amount of  
20 color fading will depend upon washing and outside exposure.  
Assuming that person washes his/her hair 4 times a week and  
exposes him/herself to outside conditions, for 2.0 hrs a  
day, the percentage of the color loss can be calculated  
using following equation.

25

Laboratory evaluation indicates that one would lose 1% of  
the color per wash and would lose about 0.75% of the  
color/hr of outside exposure.

30 % Loss of color = no. of washing X % color loss/wash + no  
of hrs. of exposure X

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% color loss/hr

$$\begin{aligned}\% \text{Loss of color per month} &= 20 \times 1.0 + 40 \text{ hrs} \times 0.75 \\ &= 20 + 30 = 50\%\end{aligned}$$

5

$$\% \text{ Loss of color per week} = 12.5\%$$

So, on average a consumer would lose 50% of the hair color. That is why most consumers want to recolor their hair every  
10 4 to 6 weeks.

With the present composition and methods, one would add color on each application of composition, according to the schedule set forth by the following mathematical formulae.

15

$$\% \text{ Color addition/week} = \text{no of conditioning treatment week} \times \text{amount color added/treatment}$$

Laboratory evaluation indicates that one would add 6 % more  
20 color per conditioning treatment.

$$\% \text{ Color addition/week} = 3 \times 10\% = 30\%$$

With new composition, we would lose 12.5% of the color but  
25 we would add 30% of the color. Due to this, one would not see any fading of the color and color stays fresh everyday.

The invention preferably relates to a method for reducing  
30 the color fading of hair to about 0 to about 10% per week,



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based on the above formulae and depending on the frequency of use.

More intense color:

5

The typical permanent color composition, upon application goes through an oxidation mechanism. Each of the dye intermediates can produce pigments through oxidation and polymerization. According to Le Chatelier's principle, the state of a chemical reaction is a dynamic state in which the chemical reaction is occurring in both directions. The rate of reaction depends upon the ratio of the rate of forward reaction to the rate of backward reaction. The higher the ratio the faster is the reaction. The factors affecting the rate of reactions are as follows:

15

1. Reactants
2. Products
3. Pressure
4. Temperature.

20

A main difference in the reaction of method of using conventional permanent color system and new invented system is the temperature. With the conventional system, the reaction takes place at room temperature, at about 70 to 75F, while with new system, since it is used in the shower, the reaction takes place at higher temperatures of about 100 to 110F. According to Le Chatelier's principle, the effect of temperature is very significant to the final rate of reaction.

30

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Under identical conditions, laboratory evaluation indicates that one would increase intensity of the color 5% with 10F-temperature difference.

5 Therefore, according to the mathematical formula just below, 15% more color is added using the compositions and methods of the invention as opposed to conventional hair coloring methods.

10 % Additional Color =  $\Delta T \times \% \text{ change in color per one degree F difference}$

$$= (100F - 70F) \times 0.5$$

$$= 30 \times 0.5 = 15\% \text{ more color due to new}$$

15 method

At the same time that hair damage is avoided by the methods of the invention, the consumer's hair is gradually being brought to the desired shade and color. This gradual change  
20 of color has two advantages: first, since the color is changed gradually, the consumer can stop the process if she does not like the color her hair is turning to. Second, some consumers do not want an abrupt change in color because they may feel embarrassed in public after having made such  
25 an abrupt change to the color of their hair. Moreover, the method and compositions of the present invention can be used in the shower, and on a daily basis, because the compositions and methods of the present invention, by contrast with current color compositions, do not employ  
30 poisonous levels of chemicals and also because compositions and methods of the present invention involve hair

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application steps that are up to about two minutes in length. By contrast current hair coloring compositions require approximately 30 minutes' time for each application, an amount of time, which is clearly not suitable for use in the shower.

The methods of the present invention are not as messy as conventional permanent hair coloring methods. The methods of the present invention do not use chemical compositions that are as smelly and noxious as those used in conventional permanent hair-coloring methods. Because the methods of the invention can be carried out in the shower, they do not involve the dripping and the mess associated with conventional permanent hair coloring. The methods of the present invention do not use chemical compositions that can stain fixtures in the bathroom or that will stain the scalp and the face. Compositions 1 and 2 upon mixture form a composition with a pleasing viscosity and that is pleasing to the fingers. This is because one or both of compositions 1 and 2 contain a cationic conditioning agent.

A dual package which can be employed in the products and kits of the present invention is U. S. Patent No. 6,082,588 to Markey et al which is hereby incorporated by reference.

25

#### KIT CONTAINING AN INSTRUCTION SHEET

The invention also relates to a kit for carrying out the hair coloring method of the invention. The kit comprises a developer solution, a dye solution and a post treatment solution, each in a separate container or in a dual

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container, as described herein. The kit also contains written instructions that explain how the compositions of the invention are used.

- 5 The consumer admixes the components of the kit according to written instructions, to obtain the aqueous reaction mixture. The admixture may be conducted in a separate vessel external to the kit, or may take place in a container of the kit adapted to provide sufficient head space for  
10 mixing. The components that are mixed are the developer composition; the dye composition. The reactants may also be admixed on the hair of the user. Essentially upon mixing, reaction of the dye and the developer will commence. After treatment for a desired time the mixture of hair developer  
15 and hair dye is removed, preferably with water or a conventional shampoo or a conventional conditioning shampoo.

As noted above, dye intermediate composition and peroxygen composition are mixed together, and the resulting mixture is  
20 applied to the hair and allowed to remain for a set time, usually about 1 to about 2 minutes to about 1 hour or more preferably about 30 minutes to about 40 minutes.

Desired change in hair color by the method of the invention  
25 is described by the mathematical formula above. Desired change in hair color can be achieved in a number of other ways. In the first instance, the consumer can compare her hair color with desired hair color or the hair color of a sample tress. Hair dyeing by the method of the invention  
30 can be repeated until her hair color matches the desired hair color. It is noted that the compositions used in the

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methods of the invention have lower contact times and thus repeated use of these compositions will not cause hair damage. An unexpected discovery of the present invention is that for damage to hair to occur, contact time in each  
5 treatment must go above the threshold value of about two minutes. Thus, the consumer can lighten or color the hair through repeated applications wherein the duration of each color application is about two minutes or less. The following two advantages are thereby achieved: first, there  
10 is a stepwise approach to the desired color; and second, a minimum of hair damage is done.

By the method of the invention, durable desired hair color, with longer lasting hair condition, clean soft feel, and a  
15 minimum of hair damage is achieved.

In following the method of the invention, the consumer can compare the color of her hair with the desired hair color, which can be printed on the package of the product. The  
20 consumer can also vary the number of days of application of the product, and the consumer can also vary the amount of time the mixture of composition 1 and 2 is left in the hair on each application. The number of applications can vary from about 7 to about 30 applications. The time of each  
25 application can vary from about 1 to about two minutes.

The method of the invention occurs over the course of days. Therefore, the final color of the consumer's hair may be affected by the amount of exposure to the sun of the hair  
30 during the course of treatment.

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Desired hair color can also be reached by comparing hair after each treatment until it matches hair tresses taken from the consumer during a prior treatment.

- 5 Desired hair color can also be reached by testing the hair after each treatment with instruments, which measure the color of the hair. When the measurements of hair color of the treated hair reach a desired level, the treatment can be stopped.

10

Indeed, reaching the desired hair color can be achieved by the use of any matching or comparison method commonly employed in the art.

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**CLAIMS:**

1. A method for permanently dyeing hair which comprises  
subjecting said hair to a number of treatments, having a  
5 set time interval between each two consecutive such  
treatments, wherein each treatment comprises steps a.)  
and b.) below:
- a.) contacting said hair, for a period of about 5  
seconds to about 5 minutes with a recently made  
10 mixture of:
- i.) an alkaline composition comprising a dye  
intermediate in a shampoo base or in a  
conditioner base; and
- ii.) an acidic composition comprising an oxidizing  
15 compound in a shampoo base or in a conditioner  
base;
- b.) rinsing said mixture from said hair with water;
- with the proviso that when a conditioner base is present  
20 in a.) i.) above, an independently selected conditioner base  
is also present in a.) ii.) above; and when a shampoo base  
is present in a.) i.) above, an independently selected  
shampoo base is also present in a.) ii.) above;
- 25 and wherein said number of treatments is between about 2  
to about 30; and wherein said set time interval between each  
two consecutive treatments is between about 8 hours and 30  
days.

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2. A method according to claim 1, wherein said dye intermediate is selected from the group consisting of m-aminophenol, p-phenylene diamine, :p-toluenediamine; p-phenylenediamine; 2-chloro-p-phenylenediamine; N-phenyl-p-phenylenediamine; N-2-methoxyethyl-p-phenylenediamine; N,N-bis-(hydroxyethyl)-p-phenylenediamine; 2-hydroxymethyl-p-phenylenediamine; 2-hydroxyethyl-p-phenylenediamine; 4, 4'-diaminodiphenylamine; 2,6-dimethyl-p-phenylenediamine; 2-isopropyl-p-phenylenediamine; N-(2-hydroxypropyl)-p-phenylenediamine; 2-propyl-p-phenylenediamine; 1,3-N, N-bis-(2-hydroxyethyl)-N, N-bis (4-aminophenyl)- 2-propanol; 2-methyl-4-dimethylaminoaniline; p-aminophenol; p-methylaminophenol; 3-methyl-p-aminophenol; 2-hydroxymethyl-p-aminophenol; 2-methyl-p-aminophenol; 2-(2-hydroxyethylaminomethyl)-p-aminophenol; 2-methoxymethyl-p-aminophenol; and 5-aminosalicylic acid; catechol; pyrogallol; o-aminophenol; 2, 4-diaminophenol; 2,4,5-trihydroxytoluene; 1,2,4-trihydroxybenzene; 2-ethylamino-p-cresol; 2,3-dihydroxynaphthalene; 5-methyl-o-aminophenol; 6-methyl-o-aminophenol; and 2-amino-5-acetaminophenol; 2-methyl-1-naphthol; 1-acetoxy-2-methylnaphthalene; 1,7-dihydroxynaphthalene; resorcinol; 4-chlororesorcinol; 1-naphthol; 1,5-dihydroxynaphthalene; 2,7-dihydroxynaphthalene; 2-methylresorcinol; 1-hydroxy-6-aminonaphthalene-3-sulfonic acid; thymol (2-isopropyl-5-methylphenol); 1,5-dihydroxy-1,2, 3,4-tetrahydronaphthalene; 2-chlororesorcinol; 2,3-dihydroxy-1,4-naphthoquinone; and 1-naphthol-4-sulfonic acid; m-phenylenediamine; 2-(2,4-



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diaminophenoxy)ethanol; N,N-bis(hydroxyethyl)-m-phenylenediamine; 2,6-diaminotoluene; N,N-bis(hydroxyethyl)-2,4-diaminophenetole; bis(2,4-diaminophenoxy)-1,3-propane; 1-hydroxyethyl-2,4-diaminobenzene; 2-amino-4-hydroxyethylaminoanisole; aminoethoxy-2,4-diaminobenzene; 2,4-diaminophenoxyacetic acid; 4,6-bis(hydroxyethoxy)-m-phenylenediamine; 2,4-diamino-5-methylphenetole; 2,4-diamino-5-hydroxyethoxytoluene; 2,4-dimethoxy 1,3-diaminobenzene; and 2,6-bis(hydroxyethylamino)toluene; m-aminophenol; 2-hydroxy-4-carbamoylmethylaminotoluene; m-carbamoylmethylaminophenol; 6-hydroxybenzomorpholine; 2-hydroxy-4-aminotoluene; 2-hydroxy-4-hydroxyethylaminotoluene; 4,6-dichloro-m-aminophenol; 2-methyl-m-aminophenol; 2-chloro-6-methyl-m-aminophenol; 2-hydroxyethoxy-5-aminophenol; 2-chloro-5-trifluoroethylaminophenol; 4-chloro-6-methyl-m-aminophenol; N-cyclopentyl-3-aminophenol; N-hydroxyethyl-4-methoxy-2-methyl-m-aminophenol and 5-amino-4-methoxy-2-methylpheno; 2-dimethylamino-5-aminopyridine; 2,4,5,6-tetra-aminopyrimidine; 4,5-diamino-1-methylpyrazole; 1-phenyl-3-methyl-5-pyrazolone; 6-methoxy-8-aminoquinoline; 2,6-dihydroxy-4-methylpyridine; 5-hydroxy-1,4-benzodioxane; 3,4-methylenedioxyphenol; 4-hydroxyethylamino-1,2-methylenedioxybenzene; 2,6-dihydroxy-3,4-dimethylpyridine; 5-chloro-2,3-dihydroxypyridine; 3,5-diamino-2,6-dimethoxypyridine; 2-hydroxyethylamino-6-methoxy-3-aminopyridine; 3,4-methylenedioxyaniline; 2,6-bis-hydroxyethoxy-3,5-diaminopyridine; 4-hydroxyindole;

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- 3-amino-5-hydroxy-2,6-dimethoxypyridine; 5,6-dihydroxyindole; 7-hydroxyindole; 5-hydroxyindole; 2-bromo-4,5- methylenedioxyphenol; 6-hydroxyindole; 3-amino-2-methylamino-6- methoxypyridine; 2-amino-3-hydroxypyridine; 2,6-diaminopyridine; 5-(3,5-diamino-2-pyridyloxy)-1,3-dihydroxypentane; 3-(3,5-diamino-2-pyridyloxy)- 2-hydroxypropanol and 4-hydroxy-2,5,6-triaminopyrimidine, or combinations thereof.
- 10 3. A method according to claim 1 or claim 2, wherein said conditioner base in a.) i.) comprises a conditioning agent independently selected from the group consisting of: dicetyl dimonium chloride; propylene glycol; poly(dimethyldiallylammonium chloride); Quaternium 57; 15 poly(dipropyldiallylammonium chloride); poly(methyl-beta-propaniodiallylammonium chloride); poly(diallylpiperidinium chloride); poly(vinylpyridinium chloride); quaternised poly(vinyl alcohol); quaternised poly(dimethylaminoethylmethacrylate); poly (N- 20 vinylpyrrolidone); poly(dimethylaminoethylmethacrylate); poly(vinyl pyridine); poly(ethyleneimine); and mixtures thereof; and wherein said conditioner base in a.) ii.) comprises a conditioning agent independently selected from the group consisting of: dicetyl dimonium chloride; 25 p[ropylene glycol; poly(dimethyldiallylammonium chloride); Quaternium 57; poly(dipropyldiallylammonium chloride); poly(methyl-beta-propaniodiallylammonium choride); poly(diallylpiperidinium chloride); poly(vinylpyridinium chloride); quaternised poly(vinyl 30 alcohol); quaternised poly (dimethylaminoethylmethacrylate); poly (N-

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vinylpyrrolidone); poly(dimethylaminoethylmethacrylate); poly(vinyl pyridine); poly(ethyleneimine); and mixtures thereof.

- 5    4. A method according to any one of claims 1 to 3, wherein said alkaline composition of a.) i.) prior to mixture with said acidic mixture of a.) ii.) has a pH of about 8 to about 10.
- 10   5. A method according to any one of claims 1 to 4, wherein said acidic composition of a.) ii.) prior to mixture with said alkaline mixture of a.) i.) has a pH of about 3 to about 5.
- 15   6. A method according to any one of claims 1 to 5, wherein said alkaline composition according to a.) i.) comprises:
- A.) from about 0.05 % to about 1.0% of a dye
- 20           intermediate;
- B.) from about 0.1% to about 0.5% of a coupler; and
- C.) from about 1 % to about 90 % of a conditioner base.
- 25   7. A method according to any one of claims 1 to 6, wherein said acidic composition according to a.) ii.) comprises:
- A.) from about 1 % to about 90 % of a conditioner
- 30           base;

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B.) from about 0.5% to about 2.5% of a volatile  
silicone; and

C.) from about 0.1 % to about 5 % of an oxidative  
compound.

5

8. A method according to any one of claims 1 to 7, wherein  
said period for contacting said hair is between about 1  
minute and 3 minutes.

10 9. A method according to any one of claims 1 to 8, wherein  
said set time interval is between about 1 day and about  
3 days.

15 10. A method according to any one of claims 1 to 9, wherein  
said hair is highlighted.

11. A method according to any one of claims 1 to 10, wherein  
said hair has wet combing tensile strength maintained.

20 12. A method according to any one of claims 1 to 11, wherein  
said hair is not significantly damaged.

13. A method according to any one of claims 1 to 12, wherein  
said hair is conditioned.

25

14. A method according to any one of claims 1 to 12, wherein  
said hair is shampooed.

30 15. A method according to any one of claims 1 to 14, wherein  
said oxidative compound is selected from the group

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consisting of hydrogen peroxide, urea peroxide, melamine peroxide, sodium perborate and sodium percarbonate.

16. A method according to any one of claims 1 to 15 wherein  
5 the first composition comprises from about 35% to about 98.9% water.

17. A method according to any one of claims 1 to 16, wherein  
the mixture of part A and part B has a neat viscosity of  
10 from about 500 cps to about 60,000 cps at 26.7.degree. C.,  
as measured by a Brookfield RVTDCP with a spindle CP-41 at  
1RPM for 3 minutes.

18. A method for maintaining hair color through the use of a  
15 permanent hair dye which comprises subjecting said hair to  
successive treatments, having a set time interval between  
each two consecutive such treatments, wherein each treatment  
comprises steps a.) and b.) below:

a.) contacting said hair, for a period of about 5  
20 seconds to about 5 minutes with a  
recently made mixture of:

i.) an alkaline composition comprising a dye  
intermediate in a shampoo base or in a conditioner  
base; and

25 ii.) an acidic composition comprising an oxidising  
compound in a shampoo base or in a conditioner  
base;

b.) rinsing said mixture from said hair with water;

30 with the proviso that when a conditioner base is present in  
a.) i.) above, an independently selected conditioner base is

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also present in a.) ii.) above; and when a shampoo base is present in a.) i.) above, an independently selected shampoo base is also present in a.) ii.) above;

5       and wherein said number of treatments is at least about 2;  
and wherein said set time interval between each two consecutive treatments is between about 8 hours and 30 days.

10   19. A method according to any one of claims 1 to 18,  
wherein said dye intermediate is present at about 0.1% to about 1%.

15   20. A method according to any one of claims 1 to 19,  
wherein said oxidative compound is present at about 2 % to about 5 %.

21. A method according to any one of claims 1 to 20 wherein said hair has combing force in the range of 5 to 55 gmforce.

20   22. A method according to claim 21 wherein said hair has combing force in the range of about 5 to 10 gmforce.

23. A method according to any one of claims 1 to 22 wherein  
25   said hair has combing index in the range of about 1.1 to 4.0.

24. A method according to claim 23 wherein said hair has combing index in the range of about 1.2 to 3.5.

30

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25. A method according to any one of claims 1 to 24 wherein said hair has break stress in the range of 0.005 to 0.03 gmforce/micron.

5 26. A method according to claim 25 wherein said hair has break stress in the range of 0.005 to 0.025 gmforce/micron.

27. A method according to claim 26 wherein said hair has break stress in the range of about 0.005 to 0.018 gmforce/micron.

10

28. A method according to any one of claims 1 to 27 wherein the ratio IR absorption at  $1040/1240\text{ cm}^{-1}$  is in the range of 0.01 to 1.5.

15

29. A method according to claim 28 wherein the ratio IR absorption at  $1040/1240$  is in the range of 0.01 to 1.0.

30. A method according to claim 29 wherein the ratio IR absorption at  $1040/1240$  is in the range of 0.01 to 0.5.

20

31. A method according to any one of claims 1 to 30 wherein said hair minimizes color fading.

25 32. A method according to any one of claims 1 to 31 wherein said hair minimizes root outgrowth.

33. A method according to any one of claims 1 to 32 wherein color added to said hair is about 4 to about 8% per treatment.

30

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34. A method according to any one of claims 1 to 33 wherein color fading to said hair is about 0 to about 10% per week.

35. A method according to any one of claims 1 to 34 wherein  
5 said composition delivers delta E of 0.1 to 65 on blonde hair

36. A method according to any one of claims 1 to 34 wherein  
said composition delivers delta E of 0.1 to 8 on brown  
10 hair.

37. A method for permanently dyeing hair which comprises  
subjecting said hair to a treatment which comprises steps  
a.) and b.) below:

- 15 a.) contacting said hair, for a period of about 5  
seconds to about 5 minutes with a  
recently made mixture of:
- A) an alkaline composition comprising a dye  
intermediate in a shampoo base or in a conditioner  
20 base; and
- B) an acidic composition comprising an oxidizing  
compound in a shampoo base or in a conditioner  
base;

b.) rinsing said mixture from said hair with water;  
25

with the proviso that when a conditioner base is present in  
A above, an independently selected conditioner base is also  
present in B above; and when a shampoo base is present in A  
above, an independently selected shampoo base is also  
30 present in B above;



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and wherein said treatment causes said hair a delta E of about 0.1 to about 40.

38. A dispenser for dispensing simultaneously composition  
5 a.) i.) and composition a.) ii.) according to any one of claims 1 to 37, which comprises:

A.) a means for holding composition a.) i.) and composition a.) ii.) in physically separate locations;

10 B.) a means for protecting composition a.) i.) and composition a.) ii.) from air prior to dispensing;

C.) a means for dispensing composition a.) i.) and composition a.) ii.) in equal amounts and in proximity to each other.

15

39. A method according to any one of claims 1 to 37, wherein composition a.) i.) and composition a.) ii.) are mixed by hand.

20 40. A method according to any one of claims 1 to 37 or 39, which comprises rinsing said mixture of composition a.) i.) and composition a.) ii.) from said hair with water in a shower.

25 41. A composition for permanently dying hair which comprises a mixture of  
Part A

a) about 0.1% to about 99.9% of a conditioning base, which comprises about 0.5% to about 5% of a quaternary  
30 nitrogen-containing conditioning agent based upon the total composition;

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- b) about 0.5 to about 10 % of a long chain fatty alcohol having about 11 to about 18 carbons in said long chain,
- c) about 0.1% to about 1% of a dye; and
- d) about 1% to about 4% of a volatile silicone;

5

## Part B

- a) about 1 to about 5% of a conditioning base;
- b) about 1 to about 5% of an oxidative compound.

10

42. A composition according to claim 41 which further comprises in part A, part B, or part A and part B, a thickener which is a high molecular weight fatty alcohol.

- 15 43. A composition according to claim 42 wherein said high molecular weight fatty alcohol is selected from the group consisting of cetyl alcohol and stearyl alcohol.

- 20 44. A composition for permanently dying hair which comprises a mixture of

## Part A

- a) about 0.1% to about 99.9% of a shampoo base; and
- b) about 0.1% to about 1% of a dye;

25 Part B

- a) about 1 to about 5% of a shampoo base;
- b) about 1 to about 5% of an oxidative compound.

- 30 45. A composition according to claim 44 wherein said shampoo base in part A comprises about 5 to about 50%,

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based on the total part A composition, of an anionic surfactant, an amphoteric surfactant, or a mixture of an anionic surfactant and an amphoteric surfactant.



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- Published:  
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(54) Title: METHOD AND COMPOSITION FOR THE GRADUAL PERMANENT COLORING OF HAIR

(57) Abstract: A method for permanently dyeing hair which comprises subjecting said hair to a number of treatments, having a set time interval between each two consecutive such treatments, wherein each treatment comprises steps a.) and b.) below: a.) contacting said hair, for a period of about 5 seconds to about 5 minutes with a recently made mixture of: i.) an alkaline composition comprising a dye intermediate in a shampoo base or in a conditioner base; and ii.) an acidic composition comprising an oxidating compound in a shampoo base or in a conditioner base; b.) rinsing said mixture from said hair with water; with the proviso that when a conditioner base is present in a.) i.) above, an independently selected conditioner base is also present in a.) ii.) above; and when a shampoo base is present in a.) i.) above, an independently selected shampoo base is also present in a.) ii.) above; and wherein said number of treatments is between about 2 to about 30; and wherein said set time interval between each two consecutive treatments is between about 8 hours and 30 days, is described.

WO 02/074266 A3

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC 7 A61K7/13

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 146 350 A (UNILEVER PLC ; UNILEVER NV (NL)) 26 June 1985 (1985-06-26) page 9, line 17 - line 20; claims; examples page 2, line 30 - page 3, line 8 ---	1-4,6,9, 15, 18-20,37
A	DE 27 04 343 A (BRISTOL MYERS CO) 18 August 1977 (1977-08-18) page 6, paragraph 2; examples page 8, paragraph 2 page 22, paragraph 2 ---	1-9,15, 18-20,37
A	US 4 402 700 A (FEINLAND RAYMOND ET AL) 6 September 1983 (1983-09-06) column 7, line 23 - line 25; claims; tables --- -/--	1-9,15, 18-20,37

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.**\* Special categories of cited documents :****"A"** document defining the general state of the art which is not considered to be of particular relevance**"E"** earlier document but published on or after the international filing date**"L"** document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)**"O"** document referring to an oral disclosure, use, exhibition or other means**"P"** document published prior to the international filing date but later than the priority date claimed**"T"** later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention**"X"** document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone**"Y"** document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.**"&"** document member of the same patent family

Date of the actual completion of the international search

22 August 2002

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## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No..
A	<p>WO 00 10515 A (UNILEVER PLC ;LEVER HINDUSTAN LTD (IN); UNILEVER NV (NL)) 2 March 2000 (2000-03-02) cited in the application page 11, paragraph 1; claims; examples -----</p>	<p>1-9,15, 18-20</p>

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/EP 02/03085

## Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2. ☒ Claims Nos.: 10-14, 16, 17, 21-36, 37 (partly), 40  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:  
see FURTHER INFORMATION sheet PCT/ISA/210.
  
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
  
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
  
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
  
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1-37, 39, 40

### Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.



## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-37,39,40

methods for dying hair (method for maintaining hair color)

2. Claim : 38

dispenser suitable for dispensing simultaneously an alkaline composition comprising a dye and a conditioner or shampoo and an acidic composition comprising an oxidizing compound and a conditioner or shampoo

3. Claims: 41-43

composition for dying hair comprising a mixture of part A:

0.1 - 99.9 % wt. conditioning base comprising 0.5 - 5 % wt.

of a quart. N-ctg. conditioning agent,

0.5 - 10 % wt. of a certain long chain fatty alcohol,

0.1 - 1 % wt. dye,

1 - 4 % wt. volatile silicone

and Part B:

1 - 5 % wt. conditioning base,

1 - 5 % wt. oxidizing compound

4. Claims: 44,45

composition for dying hair comprising a mixture of part A:

0.1 - 99.9 % wt. shampoo base,

0.1 - 1 % wt. dye

and part B:

1 - 5 % wt. shampoo base,

1 - 5 % wt. oxidizing compound

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 10-14,16,17,21-36,37 (partly),40

Present claims 10-14, 17, 21-37 relate to a method defined by reference to a desirable characteristic or property, namely that the hair is highlighted, maintains the wet combing tensile strength, is not damaged, is conditioned, is shampooed, that the mixture of part A and B has a specific neat viscosity, that the hair has a specific combing force, combing index or break stress, that a certain IR absorption ratio is achieved, that the color fading or root outgrowth is minimized, that a certain percentage of color is added or that a certain delta E is delivered.

The claims cover all methods having this characteristic or property, whereas the application provides support within the meaning of Article 6 PCT and/or disclosure within the meaning of Article 5 PCT for only a very limited number of such methods. In the present case, the claims so lack support, and the application so lacks disclosure, that a meaningful search over the whole of the claimed scope is impossible. Independent of the above reasoning, the claims also lack clarity (Article 6 PCT). An attempt is made to define the method by reference to a result to be achieved. Again, this lack of clarity in the present case is such as to render a meaningful search over the whole of the claimed scope impossible. Consequently, the search has been carried out for those parts of the claims which appear to be clear, supported and disclosed, namely those parts relating to a methods wherein a two part composition for dying hair is used. The 2 part composition comprising a part A comprising an alkaline composition comprising a dye intermediate in a shampoo or conditioner base and a part B comprising an acidic composition comprising an oxidizing compound in a shampoo or conditioner base.

Dependent claims 6 and 7 are specifying compositions a i) and a ii), however it is unclear whether they specify alkaline or acidic compositions as required by independent claim 1.

Likewise it is unclear whether parts A and B of independent product claims are alkaline or acidic compositions. Only those are supported by the description.

Claim 16 is obscure concerning the term "the first composition" as in claims 1 - 15 no first composition is mentioned. Claim 16 could therefore not be searched.

Claim 40 is obscure concerning the specification "in a shower". Such a feature cannot be considered as a limiting feature as it relates to a place where water is applied to hair. The technical feature is the rinsing with water. Whether it is done in a shower or elsewhere is irrelevant for the scope of protection.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a

## FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

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